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Some Aspects of the Tetrad Effect in the Synergic Extraction of Rare Earth β-Diketonate Adducts with *n*-Hexyl Alcohol, TBP, and TOPO

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The extraction constants of rare earth chelates, $-\log K$, and the overall stability constants of their adducts, $\log \beta$, were determined by the solvent extraction of rare earth elements such as lanthanum (III), cerium (III), neodymium (III), samarium (III), europium (III), terbium (III), ytterbium (III), and lutetium (III) with BFA (benzoyltrifluoroacetone) with or without *n*-hexyl alcohol, TBP (tri-*n*-butyl phosphate) and TOPO (tri-*n*-octylphosphine oxide) in benzene. The variation of $-\log K$ and $\log \beta$ with atomic number of rare earth elements, Z, was found to show interesting tetrad effects. Abnormal behavior of trace amounts of cerium (III) during the extraction was investigated by using various β-diketones such as AA (acetylacetone), BzA (benzoylacetone), TFA (trifluoroacetylacetone), and BFA with or without TOPO in benzene. The apparent changes of free energy, enthalpy, and entropy in the extraction of lutetium (III) with DPM (dipropionylmethane), BzA with or without TOPO in benzene were also estimated to get true information on the mechanism of the synergic extraction.

INTRODUCTION

Ten years ago, the authors reported the correlation of the ionic radius of rare earth elements such as lanthanum (III), neodymium (III), europium (III), terbium (III), and lutetium (III) with the stability constants of their benzoyltrifluoroacetonate adducts with *n*-hexyl alcohol, TBP (tri-*n*-butylphosphate), and TOPO (tri-*n*-octylphosphine oxide) in benzene.[1] After that, the "Tetrad effect" in the liquid-liquid extraction and extraction chromatography of lanthanide (III) and actinide (III) with HDOP (di *n*-octyl phosphinic acid) and DEHClMP (di 2-ethyl hexyl chloromethyl phosphonate),[2] HEHϕP (*n*-heptane-2-ethyl hexyl phenyl phosphonic acid) and HDEHP (bis 2-ethyl hexyl phosphoric acid)[3] have been found and generalized on the basis of the following hypothesis: "In systems involving all 15 lanthanides (III), the points on a plot of the logarithm of a suitable numerical measure of a given property of these elements *vs.* Z may be grouped, through the use of four smooth curves without inflections, into four tetrads with the gadolinium point being common to the second and third tetrads and the extended smooth curves intersecting additionally, in the 60–61 and 67–68 Z regions. In a similar plot for actinides (III), an analogous tetrad effect is apparent with the curium point being common to the second and third tetrads". Tetrad effects in the synergic extraction of rare earth elements with TTA (thenoyltrifluoroacetone) in the presence of TBP and DBSO (di-*n*-butyl sulphoxide) have

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also been reported.[4,5] The present authors have attempted to search for the tetrad effect by reexamining the synergic extraction data on the rare earth benzoyltrifluoroacetonate adducts with *n*-hexyl alcohol, TBP, and TOPO in benzene including new data on cerium (III), samarium (III), and ytterbium (III). In order to get more real information on the synersism, the apparent values of free energy, enthalpy, and entropy in the complex formation of lutetium (III) β-diketonates of DPM (dipropionylmethane), BzA (benzoylacetone), and BFA (benzoyltrifluoroacetone) with or without TOPO in benzene have also been reexamined by using the previous data.[6]

EXPERIMENTAL

Materials and experimental procedures were already described in the previous papers.[1,6] The radioisotopes, cerium-144 was purchased from The Radiochemical Centre, Amercham, England; and samarium-145 and ytterbium-169 were produced in the Research Reactor of Kyoto University. Before the measurements of the gamma activities of cerium-144, both phases after the extraction were allowed to stand for several hours till the radioactive equilibrium of cerium-144 and praseodymium-144 had been established.

RESULTS AND DISCUSSION

Tetrad Effect in Lanthanide (III)-BFA-*n*-Hexyl Alcohol, TBP, and TOPO-Benzene Extraction System

The extraction constants of rare earth chelates, $-\log K$, *vs.* atomic number of the rare earth elements on the extraction of their benzoyltrifluoroacetonates in benzene are shown in Fig. 1, as smooth curves with a dotted line. Tetrad effect was observed on four concave curves drawn through the points. The overall stability constants of rare earth benzoyltrifluoroacetonate adducts with *n*-hexyl alcohol, TBP, and TOPO in benzene, $\log\beta$, are also plotted as a function of atomic number of rare earth elements in Fig. 1. Four convex curves

Table I. Extraction Constants of Rare Earth Benzoyltrifluoroacetonates, $-\log K$, and Overall Stability Constants of Their Adducts with *n*-Hexyl Alcohol, TBP, and TOPO in Benzene

		La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
$-\log K$		11.6	9.5	9.9	8.1	8.9	8.8	7.8	7.7
$\log\beta$	*n*-Hexyl alcohol	3.80		3.87		3.50	3.50		3.10
	TBP	8.50		8.45	8.05	7.80	7.76	7.05	6.40
	TOPO	13.00	11.45	12.55		11.86	11.76		7.83*

* Formation of the second adduct, Lu $(BFA)_2(TOPO)_2$ was not observed. The values in the adduct formation were determined by analyzing the curves of $-\Delta$ $pH_{1/2}$ (the values of the $pH_{1/2}$ shift) *vs.* log (organic base)$_0$ plots.

$$K=(MR_3)_0(H^+)^3/(M^{3+})(HR)_0^3$$

$$\beta=(MR_3L_2)_0/(MR_3)_0(L)_0^2$$

where ( ) and ( )$_0$ designate the concentration of chemical species in aqueous phase and in organic phase, respectively.

M^{3+}: Rare earth ions HR: β-Diketones L: Organic bases

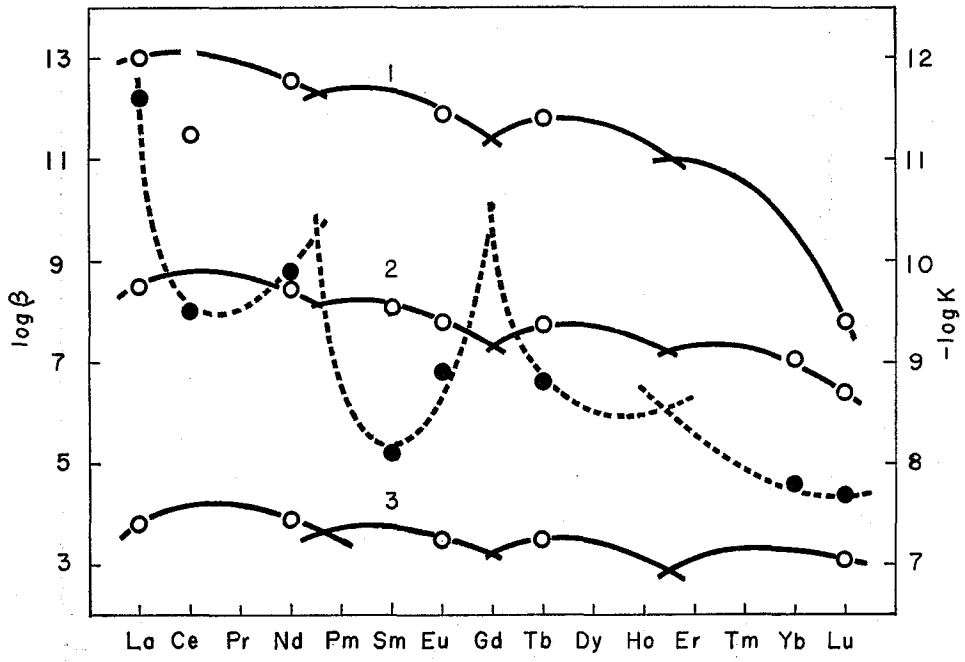

Fig. 1. The extraction constants of rare earth benzoyltrifluoroacetonates, —log K, and the overall stability constants of their adducts with *n*-hexyl alcohol, TBP, and TOPO in benzene, log β, as a function of atomic number of rare earth elements.
Organic bases: —●— none, —○— 1 TOPO, 2 TBP, 3 *n*-Hexyl alcohol

appeared with the increase in the atomic number of rare earth elements except cerium (III). Extraction constants of rare earth benzoyltrifluoroacetonates, $-\log K$, and overall stability constants of their adducts with *n*-hexyl alcohol, TBP, and TOPO in benzene, log β, are summarized in Table I. These results suggest that the behavior of rare earth elements in lanthanide (III)-BFA-*n*-hexyl alcohol, TBP, and TOPO-benzene extraction systems may be interpreted in terms of the tetrad effect.

Abnormal Behavior in Cerium (III)-BFA-TOPO-Benzene Extraction System

In order to get true information on the synergic extraction of cerium (III) benzoyltrifluoroacetonate adducts with TOPO, the extractions of trace amounts of cerium (III) were carried out with other various β-diketones with or without TOPO in benzene. Figure 2 shows the logD *vs.* pH plots in the extraction of trace amounts of cerium (III) with AA (acetylacetone), BzA (benzoylacetone), TFA (trifluoroacetylacetone), and BFA (benzoylacetone). Cerium (III) can be extracted in the lower pH region by using β-diketones with a fluoromethyl group. This fact is caused by the inductive effect of the fluoromethyl group, which rises the acidity of the enol form. In the extraction of cerium (III) with β-diketones which are comparatively soluble in water, the slopes of the logD *vs.* pH plots deviate from 3, the theoretical value, because of the formation of water-soluble complexes. However, the extraction behavior of cerium (III) was strange, because the slopes of the logD *vs.* pH plots were 3.0 for AA, 2.2 for BFA, 2.0 for BzA, and 1.4 for TFA, respectively. In the AA extraction system, it is generally said that trace amounts of

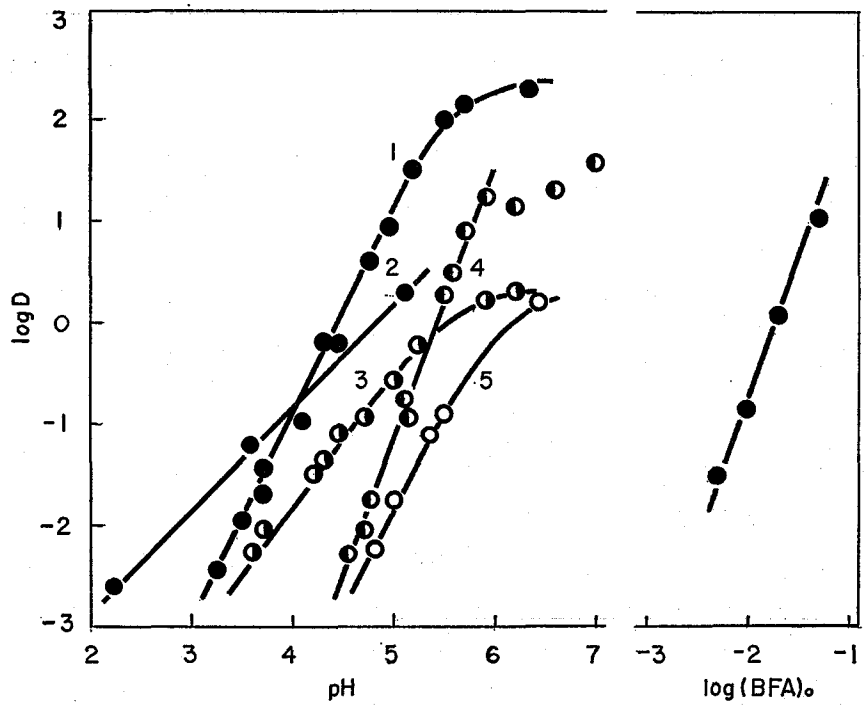

Fig. 2. Logarithm of the distribution ratio of trace amounts of cerium (III) as a function of the pH value and BFA concentration.
Organic phase: 1, $2;5\times10^{-2}$ M BFA, $3;5\times10^{-2}$ M TFA, $4;10^{-1}$ M AA, $5;10^{-1}$ M BzA
Aqueous phase: 1, 3, 4, $5;10^{-1}$ M $NaClO_4$, $2;10^{-1}$ M $NaBrO_3$
Solvent: Benzene Shaking time: 1 hour

cerium (III) exists as tetravalent ion, and the chemical form extracted may be of $CeA_4 2HA$ complex.[7,8] In the case of BFA extraction system, the logD *vs.* log $(BFA)_0$ plots gave the slope of 3, indicating the formation of Ce $(BFA)_3$ complex. The effects of the functional groups of various β-diketones on the adduct formation between cerium (III) chelates and TOPO in benzene are shown in Fig. 3 as logD*/D *vs.* log $(TOPO)_c$ plots. The straight lines with a slope of 2 in high concentration of TOPO indicate that two molecules of TOPO bind one molecule of the metal chelate in Ce (III)-BFA and TFA-TOPO-benzene extraction systems. The synergism in Ce(III)-BzA and AA-TOPO-benzene extraction systems was not observed. These facts suggest that cerium in a cerous state can preferably be extracted with the ligands having fluoromethyl group to form trivalent cerium chelate, while cerium in a ceric state can be extracted with ligands without fluoromethyl group to form tetravalent cerium chelates. Even after oxidizing a trace amount of cerium (III) in the presence of 0.1 M sodium bromate, cerium can also be extracted with BFA with or without TOPO in benzene as shown in Fig. 2 and Fig. 3, respectively. However, the slope of logD *vs.* pH plots gave the lower value, and TOPO showed the smaller synergic effect. The extraction of trace amounts of cerium (III) with β-diketones may depend on the cerous-ceric equilibrium, hydrolysis of cerium ions, and the rate of their complex formation with ligands during the extraction.

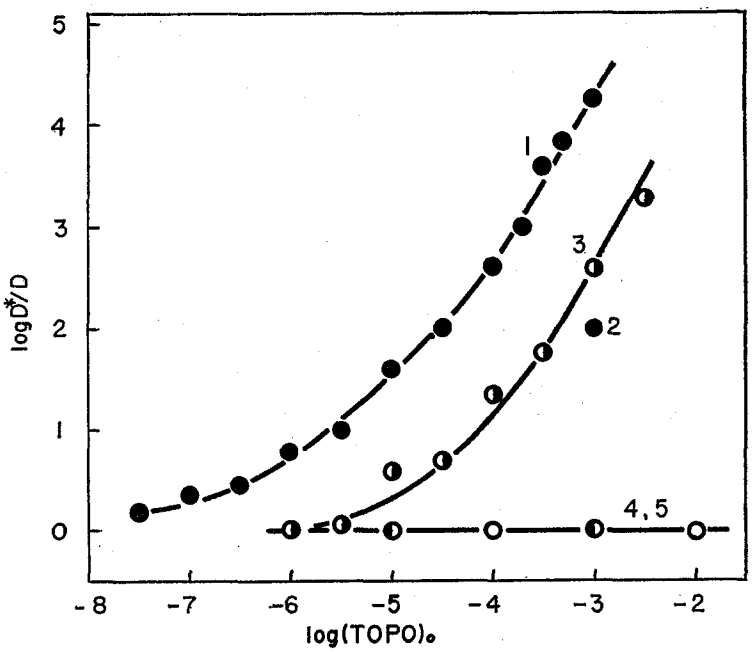

Fig. 3. Variation of the distribution ratio of rare earth elements as a function of TOPO concentration. The symbols in figure are the same as in Fig. 2.

Free Energy, Enthalpy and Entropy in the Complex Formation of Lutetium (III)-DPM, BzA, and BFA-TOPO Benzene Extraction System

The apparent changes of free energy, enthalpy, and entropy in the extraction of lutetium (III) with DPM (dipropionylmethane), BzA, and BFA with or without TOPO in benzene were also estimated, and these results were presented in Table II. Judging from the data in the table, it is clear that the adduct formation is favored by the enthalpy and opposed by entropy changes. The apparent enthalpy change ($-\Delta H$ kcal/mol) on the

Table II. Thermodynamic Values for the Extraction of Lutetium (III) with DPM, BzA, and BFA with or without TOPO in Benzene

Species	$-\log K$	$\log \beta$	ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/deg/mole)
$Lu(BFA)_3$	7.69		4.48	6.16	5.73
$Lu(BFA)_3TOPO$		7.50	−4.40	−8.62	−14.39
$Lu(BzA)_3$	15.21		8.86	11.92	10.44
$Lu(BzA)_3TOPO$		5.25	−3.11	−5.89	−9.48
$Lu(DPM)_3$	16.57		9.65	8.25	−4.78
$Lu(DPM)_3TOPO$		4.35	−2.55	−5.46	−9.93

$\Delta G = -RT \log F = \Delta H - T\Delta S$

where $\log F$ is $\log K$ or $\log \beta$. ΔG, ΔH, and ΔS indicate the changes of free energy, enthalpy, and entropy, respectively.

R: 1.987 cal/deg mole $T = 273.16 + t°C$

adduct formation between lutetium chelates and TOPO in benzene is 5.5–8.6 Kcal/mole, which is equivalent to hydrogen bonding. The expansion of coordination number of lutetium (III) may be more real mechanism in the synergic extraction as has recently been pointed out in the synergic extraction of europium (III) and thulium (III) with TTA in the presence of TBP and AA.[9]

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